

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) PRODUCTION OF LOWER ALIPHATIC MERCAPTANS

- (71) We, DEUTSCHE GOLD- UND SILBER - SCHEINDEANSTALT Vormals Roessler of 9 Weissfrauenstrasse, Frankfurt/Main, Germany, a body corporate organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the production of lower alkyl mercaptans, i.e. methyl, ethyl, propyl and butyl mercaptans, and preferably methyl mercaptan.
- It is known that methyl mercaptan can be prepared by catalytically reacting methanol or dimethyl ether with hydrogen sulphide. In this process, thorium oxide (U.S. Patent Specification 2,685,505), aluminium oxide (German Patent Specification 1,134,368) and aluminium oxide activated with different substances (U.S. Patent Specifications 2,820,061/062/063, German Patent Specification 1,151,796) for example, are used as catalysts. Potassium tungstate on γ -aluminium oxide in particular promotes the formation of methyl mercaptan (*loc. cit.*). This catalyst is not only active, it is also largely specific for the preparation of methyl mercaptan.
- Particular difficulties are encountered in working up the reaction mixture with consists of unreacted starting materials, the mercaptan, the corresponding dialkyl sulphide and dialkyl ether and also water and inert gases.
- In the case of methyl mercaptan, the mixture consists of hydrogen sulphide and methanol and water, methyl mercaptan and the dimethyl sulphide and dimethyl ether formed as secondary products, and also of the gases which take no part in the reaction and are thus inert in the context of the reaction, for example methane, carbon monoxides, hydrogen and nitrogen. Product fractions that are still present in the hydrogen sulphide separated off are lost through several successive fractional distillations and absorptions at elevated pressure. Some of the hydrogen sulphide has
- to be removed from the process circuit to prevent the inert products from accumulating in the recycled hydrogen sulphide (U.S. Patent Specification 2,808,441). Neither is it possible to recover a mercaptan that is free from hydrogen sulphide in the working up by absorption described above. It is known from German Patent Specification 1,134,368 that the reaction yielding methyl mercaptan and the working up of the reaction mixture can be carried out at extremely high pressures, preferably at pressures of from 17.5 to 24.5 atms. Considerable outlay in terms of energy and high-pressure apparatus is required for this purpose. In addition to this, losses of methyl mercaptan and hydrogen sulphide are incurred through the greater degree of solubility in water at the elevated pressure so that certain amounts of the aforementioned substances are discharged with the effluent.
- The object of the invention is to restrict these losses, to recover the mercaptan containing less than 0.02% of hydrogen sulphide in substantially quantitative yields and to avoid effluents which cannot be discharged into canals or rivers without having to be worked up at considerable cost.
- It has now been found that aliphatic mercaptan substantially free from hydrogen sulphide can be obtained in substantially quantitative yields with little technical outlay by the process according to the invention.
- The present invention provides a process for working up products in a process for the production of an alkyl mercaptan with 1 to 4 carbon atoms by reacting the corresponding primary alkyl alcohol with hydrogen sulphide under pressure in the presence of a catalyst, wherein the gas mixture accumulating after the reaction and consisting of hydrogen sulphide, unreacted alcohol alkyl mercaptan, dialkyl sulphide, water, dialkyl ether and inert gases is separated in a separation column in the form of a packed column or a plate column, into volatile and non-volatile fractions under a pressure of at most 10 atms. and preferably from 5 to 10 atms., and at a temperature of [Price 25p]

- from 10 to 140°C., after which the entrained non-volatile fractions, primarily alkyl mercaptan and dialkyl sulphide are washed out of the said volatile fraction optionally after this has been cooled, by means of a washing agent flowing in counter current to the said volatile fraction in the upper part of the separation column or in a separate washing column, the said entrained non-volatile fractions together with the washing agent are returned to the said separation column and, following removal of the hydrogen sulphide and the ether, are worked up together with the initial non-volatile fraction in further columns.
- The readily volatile fraction is composed of hydrogen sulphide, dialkyl ether and inert gas and the non-volatile fraction water, alcohol, alkyl mercaptan and dialkyl sulphide. The washing liquids laden with alkyl mercaptan and dialkyl sulphide which also contain some hydrogen sulphide and dialkyl ether in solution, are recycled to the separation column in cases where a separate washing column is used. If only one column is used, the laden washing liquids from the upper part of the separation column flow in counter current to the ascending gas mixture before they reach the sump.
- In both cases, hydrogen sulphide and dialkyl ether are removed by the counter flowing vapours and flow either into the separate washing column or into the upper part of the separation column. Hydrogen sulphide, dialkyl ether and the inert gases are removed free from mercaptan and dialkyl sulphide from the washing column or the upper part of the separation column, and for the most part may be recycled to the reactor. In this case a small fraction has to be separated out and burnt or otherwise processed to prevent the inert materials from accumulating in too high a concentration. The size of this component stream is governed by the purity of the hydrogen sulphide used for the reaction. The purer the hydrogen sulphide, the smaller will be the quantity that has to be separated out. A small portion of these inert materials is formed during the reaction as a result of slight decomposition of the methanol.
- A major advantage of the process according to the invention is that as early as in the first stage alkyl mercaptan and hydrogen sulphide are quantitatively separated by combined stripping and washing. Accordingly, there is no alkyl mercaptan in the gas mixture flowing off overhead, nor any hydrogen sulphide in the sump. At the same time, most of the alkyl ether formed as secondary product during the reaction, together with the hydrogen sulphide, is recycled to the reactor where it is reacted to form alkyl mercaptan. The yield is thus increased and the amount of energy required minimal.
- As already mentioned, packed columns and plate columns may be used for this process. Separation may be carried out both in a column with a lower section for stripping and an upper section for washing or alternatively in two individual columns. Cooling is carried out either inside the column or in a separate condenser.
- Suitable washing agents include solvents or solvent mixtures that are miscible with water such as aliphatic alcohols with 1 to 4 carbon atoms, especially commercial methanols of varying quality of the kind used in the preparation of methyl mercaptan, and also water-immiscible solvents and solvent mixtures with a low vapour pressure such as, for example, aliphatic, cycloaliphatic or aromatic hydrocarbons or mixtures thereof which boils above 160°C. and is difficult to crack, high-boiling alcohols, esters or ethers. Alkylated benzenes with boiling points above 160°C. are particularly suitable. Finally, water itself may also be used as the washing agent.
- According to one advantageous embodiment of the invention the alkyl mercaptan produced is methyl mercaptan and methanol accumulating after the non-volatile product of the separation column has been worked up is used as a starting material for the production of the alkyl mercaptan. In this case the washing agent is preferably commercial methanol and the starting material for the production of methyl mercaptan is methanol derived from the working up of the non-volatile product of the separation column.
- The invention is discussed in detail in the following description which is exemplary of the preparation of methyl mercaptan, reference being made to the accompanying flow sheet.
- A gas mixture issuing from a reactor is introduced through pipe 10 into the lower part 1b of column 1 which also has an upper section 1a, and is separated into a gaseous phase which consists predominantly of hydrogen sulphide, inert gases, dimethyl ether and methyl mercaptan and which rises into the upper section 1a of the column, and into a liquid sump phase consisting of methyl mercaptan, dimethyl sulphide, methanol, water and washing agent, which runs off from the bottom section 1b. The column is heated by the heat exchanger 1d, whilst the gas flowing off and the recycled component are cooled and condensed by 1c.
- The gas mixture rising into the upper section 1a of the column still contains some methyl mercaptan and dimethyl sulphide which, corresponding to their vapour pressures, are entrained beyond the condenser 1c. In order to remove them, the washing agent is introduced through the pipe 13, flowing in counter current to the gas through the column packing or plates, absorbing methyl mercaptan and dimethyl sulphide as it does so. The washing agent carries them into section 1b. Hydrogen sulphide and dimethyl ether are separated from the washing agent in this lower part of the column so that the washing agent accumulates.

lates as sump product free from hydrogen sulphide together with methyl mercaptan, dimethyl sulphide, water and methanol.

This sump product is introduced via conduit 5 12 into the centre part of the column 2 which is also in the form of a plate or packed column heated with a heat exchanger 2d and provided with a condenser 2c. Methyl mercaptan and dimethyl sulphide flow off overhead, whilst 10 methanol, water and washing agent accumulate as sump products.

Methanol goes over with the head product corresponding to the compositions of the azeotropic mixtures, dimethyl sulphide/methanol 15 and methyl mercaptan/methanol. If the presence of methanol in the products methyl mercaptan and dimethyl sulphide is troublesome, the aforementioned azeotropes may be separated by extractive distillation by the additional introduction of water into the upper section 20 of the column 2.

If, however, the presence of methanol in the end product, methyl mercaptan, does not cause any problems, the end product may contain 25 as much methanol as corresponds to the composition of the azeotrope, that is to say approximately 1 to 2% of methanol in methyl mercaptan. Small quantities of water always flow off at the upper end of the column 2 30 and 3.

The head product from column 2 is purified by distillation in another packed column or plate column 3 into which it is delivered through the pipe 20. Column 3 is heated by 35 a heat exchanger 3d and provided with a condenser 3. Methyl mercaptan accumulates in a purity above 98% and in a purity in excess of 99.6% where water is additionally introduced into column 2, and contains less than 40 0.02% of hydrogen sulphide.

The method by which the washing agent is recovered is governed by the nature of the washing agent itself. In every case, however, the washing agent is worked up together with 45 the sump products from column 1 and 2 rather than separately, in contrast to the prior art (cf. for example Ind. Eng. Chem., Vol. I, pages 271 to 276) (1962).

In cases where a washing agent miscible 50 with water, such as methanol, is used, the sump product from column 2 is delivered through the pipe 40 to a packed column or plate column 4 which is provided with heat exchangers 4c and 4d and separated into the 55 mixture of washing agents and methanol flowing off overhead and into the water formed during the reaction which is run off as sump product. This effluent is free from hydrogen sulphide, methyl mercaptan and other strong-smelling substances and can be discharged into canals or rivers.

The washing agent containing the small amount of unreacted methanol is returned to the head of the column 1a through the pipes 60 41, 42 and 13. It carries any strong-smelling

substances still present with it. If the washing agent used is methanol itself, the quantity required for the reaction can preferably be taken from the washing agent circuit through the pipe 41. This quantity is then replaced by 70 fresh commercial methanol through pipe 13. In cases where the washing agent used is not miscible with water, the sump product from column 2 is separated after cooling in a phase-separating vessel (not shown). The washing agent may immediately be returned to column 1. In cases where it is desired to recover the small quantity of methanol present in the water emanating from the reaction, the water is distilled free from methanol and also free from any odour in known manner and with a limited energy requirement.

In cases where water is used as a washing agent, a fraction corresponding to the water of reaction is separated off after leaving the sump product from column 2. Since this fraction contains small quantities of methanol and strong-smelling substances, it is freed from them in a small column (not shown). The remaining part of the sump product may be reused for washing in column 1b after it has been cooled.

EXAMPLE

The process is illustrated in the following with reference to the preparation of methyl mercaptan.

A mixture issuing from a reactor with the composition 36.1% by weight of hydrogen sulphide, 2.5% by weight of methanol, 38.4% by weight of methyl mercaptan, 1.5% by weight of dimethyl ether, 2.7% by weight of dimethyl sulphide, 15.6% of water and 3.2% by weight of inert gases was introduced through pipe 10 into the lower part 1b of the column 1 at a pressure of 7 atms. 2.5 kg of methanol were delivered for washing to the head of the washing column per kilogram of methyl mercaptan. The temperature at the head of section 1a of the column was 25°C, 48°C below the condenser and 92°C in the sump (of section 1b of the column). No methyl mercaptan and no dimethyl sulphide could be detected in the gas flowing off from the head of column 1a which consisted mainly of hydrogen sulphide.

The sump product from the first column was delivered into the second column. 2.3 kg of water were delivered through a pipe 21 just below the head of this column per kilogram of methyl mercaptan. The column operated at a pressure of 7 atms. and had a sump temperature of 149°C and a head temperature of 72°C. The sump product of this column was separated in a column 4 operating at normal pressure. The effluent (43) of this column was odourless water. Some of the head product was used for delivery into the reactor, and the rest for washing in column 1b. The fraction branched off for the reactor 6 (through pipe 41) was replaced by fresh methanol (13) for

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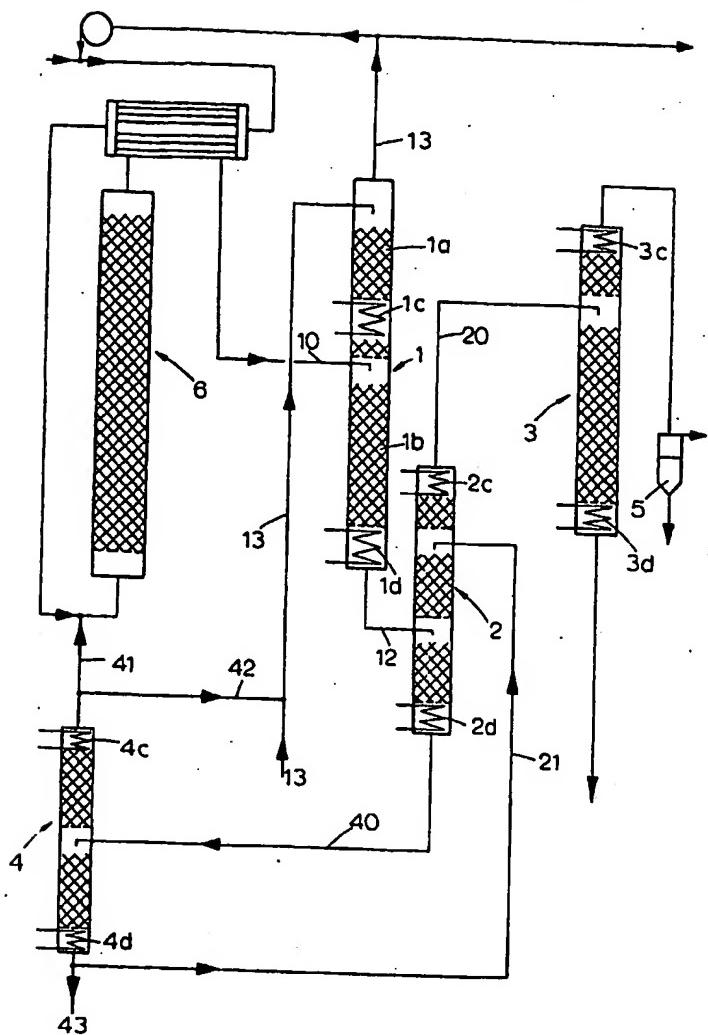
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- washing in column 1. Methyl mercaptan was obtained from the head product of the second column after repeated distillation in column 3. After it had passed through a water separator 5, it still contained 0.015% by weight of hydrogen sulphide and 0.15% by weight of methanol.
- WHAT WE CLAIM IS:—**
1. A process for working up the products in a process for the production of an alkyl mercaptan with 1 to 4 carbon atoms by reacting the corresponding primary alkyl alcohol with hydrogen sulphide under pressure in the presence of a catalyst, wherein the gas mixture accumulating after the reaction and consisting of hydrogen sulphide, unreacted alcohol, alkyl mercaptan, dialkyl sulphide, water, dialkyl ether and inert gases is separated in a separation column in the form of a packed column or plate column into volatile and non-volatile fractions under a pressure of at most 10 atmos. and at a temperature of from 10 to 140°C, after which the entrained non-volatile fractions, primarily alkyl mercaptan and dialkyl sulphide, are washed out of the said volatile fraction by means of a washing agent flowing in counter current to the said volatile fraction in the upper part of the separation column or in a separate washing column, the said entrained non-volatile fractions together with the washing agent are returned to the said separation column and, following removal of the hydrogen sulphide and the ether, are worked up together with the initial non-volatile fraction in further columns.
 2. A process as claimed in claim 1, wherein a solvent or solvent mixture miscible with water is used as the washing agent.
 3. A process as claimed in claim 2, wherein the washing agent is an aliphatic alcohol with 1 to 4 carbon atoms.
 4. A process as claimed in claim 3, wherein the washing agent is commercial methanol.
 5. A process as claimed in claim 1, wherein a solvent or solvent mixture immiscible with water is used as the washing agent.
 6. A process as claimed in claim 5, wherein the washing agent is an aliphatic, cycloaliphatic or aromatic hydrocarbon or mixture thereof.
 7. A process as claimed in claim 6, wherein a hydrocarbon or hydrocarbon mixture which boils at above 160°C and which is difficult to crack is used as the washing agent.
 8. A process as claimed in claim 1, wherein water is used as the washing agent.
 9. A process as claimed in any of claims 1 to 8, wherein the separation column operates under a pressure of from 5 to 10 atmos.
 10. A process as claimed in any of claims 1 to 9, wherein the alkyl mercaptan produced is methyl mercaptan and methanol accumulating after the non-volatile product of the separation column has been worked up is used as a starting material for the production of the alkyl mercaptan.
 11. A process as claimed in claim 10, wherein the washing agent is commercial methanol and the starting material for the production of methyl mercaptan is methanol derived from the working up of the non-volatile product of the separation column.
 12. A process as claimed in claim 10 or 11, wherein, during the working up process, azeotropic mixtures of methanol/methyl mercaptan and methanol/dimethyl sulphide are separated by extractive distillation with the aid of water as washing agent.
 13. A process for working up the gas mixture obtained in a process for the production of an alkyl mercaptan substantially as hereinbefore described with reference to the accompanying drawing and/or the Example.
 14. An alkyl mercaptan when produced by a process as claimed in any of claims 1 to 13.

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1268842 COMPLETE SPECIFICATION

1 SHEET This drawing is a reproduction of
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/09432

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B17/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 17 68 826 B (DEGUSSA) 26 August 1971 (1971-08-26) column 3, line 6 - line 31; claims; figure	1-8
A	US 2 479 781 A (ROBINSON SAM P) 23 August 1949 (1949-08-23)	
A	US 2 784 055 A (LEONARD SILVER) 5 March 1957 (1957-03-05)	
A	US 5 866 721 A (GOEDECKE RALF ET AL) 2 February 1999 (1999-02-02)	

Further documents are listed in the continuation of box C.

Patient family members are listed in annex.

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Date of the actual completion of the International search	Date of mailing of the International search report
3 December 2003	11/12/2003
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel: (+31-70) 340-2040, Tx: 31 651 epo nl, Fax: (+31-70) 340-3018	Authorized officer Zalm, W

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/09432

Patent document cited in search report	Publication date	Patent family member(s)		Publication date	
DE 1768826	B	26-08-1971	DE AT BE CH FR GB JP NL RO YU	1768826 B1 289048 B 735619 A 525199 A 2012271 A5 1268842 A 50024939 B 6907265 A ,B 56554 A1 165569 A ,B	26-08-1971 25-03-1971 16-12-1969 15-07-1972 20-03-1970 29-03-1972 20-08-1975 06-01-1970 11-11-1974 31-10-1974
US 2479781	A	23-08-1949	NONE		
US 2784055	A	05-03-1957	DE	955319 C	
US 5866721	A	02-02-1999	DE BR CN DE EP ES JP RU	19654516 C1 9706467 A 1189487 A ,B 59703013 D1 0850923 A1 2154874 T3 10195041 A 2178411 C2	01-10-1998 01-06-1999 05-08-1998 29-03-2001 01-07-1998 16-04-2001 28-07-1998 20-01-2002

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